

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 October 2002 (03.10.2002)

PCT

(10) International Publication Number
WO 02/077356 A1

(51) International Patent Classification⁷: D06L 1/02, 1/04,
C11D 11/00, D06F 43/00, C11D 7/50 // 3/16

(21) International Application Number: PCT/US02/04620

(22) International Filing Date: 15 February 2002 (15.02.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/813,666 21 March 2001 (21.03.2001) US

(71) Applicant: GENERAL ELECTRIC COMPANY
[US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventors: PERRY, Robert, J.; 2115 Niskayuna Drive,
Niskayuna, NY 12309 (US). HUBBARD, Patricia, A.; 19
Crestview Drive, West Sand Lake, NY 12196 (US).

(74) Agents: WINTER, Catherine, J. et al.; General Electric
Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431
(US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GI,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GI, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: VAPOR PHASE SILOXANE DRY CLEANING PROCESS

(57) Abstract: The process of the present invention is directed to a dry cleaning process, comprising the use of volatile cyclic, linear or branched siloxanes in the vapor phase for the cleaning of soiled or stained fabrics. The linear or branched siloxanes have the formula: $M_{2x+y+z}D_zT_yQ_z$, wherein: M is $R^1_3SiO_{1/2}$; D is $R^2R^3SiO_{2/2}$; T is $R^4SiO_{1/2}$; and Q is $SiO_{4/2}$. R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical having from one to forty carbon atoms; and x and y are each integers, wherein $0 < x < 10$ and $0 < y < 10$, and $0 < z < 10$. While the cyclic siloxanes have the formula (1) wherein R^5 , R^6 , R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and a and b are each integers wherein $0 < a < 10$ and $0 < b < 10$, provided that $3 < (a + b) < 10$.

WO 02/077356 A1

BEST AVAILABLE COPY

SUMMARY OF THE INVENTION

The process of the present invention is directed to a cleaning process, comprising the use of a volatile cyclic, linear or branched siloxane in the vapor phase for the cleaning of articles.

Further, the present invention provides for a process for cleaning soiled
5 articles of manufacture comprising:

- a) contacting the soiled article of manufacture with a vapor phase silicone compound;
- b) allowing the vapor phase silicone compound in contact with the soiled
10 article of manufacture to condense to the liquid phase becoming thereby a condensed silicone liquid; and
- c) draining the condensed silicone liquid away from the article of manufacture whereby the soiled article of manufacture is cleaned.

In another embodiment the present invention provides for a process for cleaning soiled garments comprising:

- 15 a) contacting the soiled garment with a vapor phase silicone compound;
- b) allowing the vapor phase silicone compound in contact with the soiled garment to condense to the liquid phase becoming thereby a condensed silicone liquid; and
- c) draining the condensed silicone liquid away from the garment whereby
20 the soiled garment is cleaned.

and Q is $\text{SiO}_{4/2}$

R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical having from one to forty carbon atoms; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

5 Suitable monovalent hydrocarbon groups include linear hydrocarbon radicals, branched hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic or fluoro containing hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

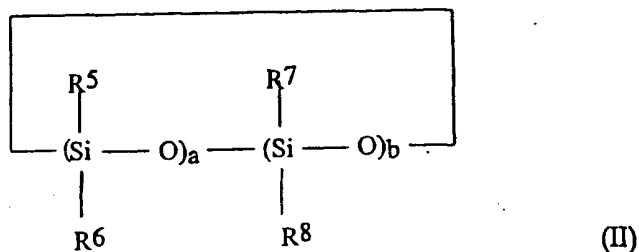
10 As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

15 As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic or fluoro containing rings per group, which may optionally be substituted on the one or more aromatic or fluoro containing rings, preferably with one or more (C₁-C₆)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

20 As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenyloxypropyl, biphenyloxypropyl.

ranging from 0.01 to 760 mm Hg at a temperature ranging from about 10 °C to about 300 °C.

In another embodiment, the cyclic siloxane comprises one or more compounds of the structural formula (II):



wherein:

R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

In yet another embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane. In yet another embodiment, the cyclic siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of alkylhalosilanes, e.g. dimethyldichlorosilane, and are commercially available.

the process of the present invention is performed at a pressure that is varied among the steps of the process, e.g. initially contacting the garment to be cleaned with a vapor at a pressure below atmospheric followed by raising the pressure to atmospheric pressure to condense the vapor in the garment and
5 allow the cleaning fluids to drain away from the garment.

Alternatively, the articles remain in the cleaning vessel and the silicone or silicone containing solvent is removed by various means and the articles are dried in the cleaning vessel as is commonly seen in typical dry cleaning machines.

10 An article, such as for example, a textile or leather article, typically, a garment, is cleaned by contacting the article with the vapors of the composition of the present invention. In a preferred embodiment, the articles to be cleaned include textiles made from natural fibers, such as for example, cotton, wool, linen and hemp, from synthetic fibers, such as, for example,
15 polyester fibers, polyamide fibers, polypropylene fibers and elastomeric fibers, from blends of natural and synthetic fibers, from natural or synthetic leather or natural or synthetic fur.

The article and dry cleaning composition are then separated, by, for example, one or more of draining and centrifugation. In a preferred
20 embodiment, separation of the article and dry cleaning composition is followed by the application of heat, preferably, heating to a temperature of from 15°C to 120°C, preferably from 20°C to 100°C, or reduced pressure, preferably, a pressure of from 1 mm Hg to 750 mm Hg, or by application of both heat and reduced pressure, to the article.

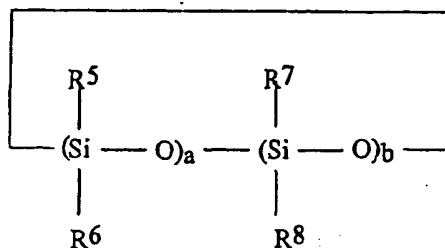
25 Testing for oil soluble stain removal was accomplished using a blue 50/50 cotton/poly cloth and a red satin fabric. The approximately 2 inch square samples were stained with motor oil, suspended by wires in a large

was reduced to 1-2 mm Hg and the temperature of the solvent reservoir was raised to 70-80 °C. The vapors were allowed to contact the stained fabrics for 5 minutes. After this time, the heat was removed, the vessel cooled and the samples removed and air dried and evaluated. All traces of the oil were removed from both fabrics. No extraction of the red dye from the satin fabric was observed.

Example 3 - Reduced Pressure, linear solvent

Samples of red satin and blue cotton/poly fabrics were treated with motor oil which was allowed to stain for 18 hours then attached to a wire holder and suspended above a reservoir of MD2M. The pressure in the system was reduced to 1-2 mm Hg and the temperature of the solvent reservoir was raised to 70-80 °C. The vapors were allowed to contact the stained fabrics for 5 minutes. After this time, the heat was removed, the vessel cooled and the samples removed and air dried and evaluated. All traces of the oil were removed from both fabrics. No extraction of the red dye from the satin fabric was observed.

3. The process of claim 1 wherein the silicone compound has the formula:



wherein:

- 5 R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

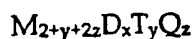
4. The process of claim 2 wherein each of the steps a), b) and c) are independently conducted at a temperature ranging from about 10 °C to about 10 300 °C.

5. The process of claim 3 wherein each of the steps a), b) and c) are independently conducted at a temperature ranging from about 10 °C to about 300 °C.

6. The process of claim 4 wherein each of the steps a), b) and c) are 15 independently conducted at a pressure ranging from about 0.01 mm Hg to about 760 mm Hg.

7. The process of claim 5 wherein each of the steps a), b) and c) are independently conducted at a pressure ranging from about 0.01 mm Hg to about 760 mm Hg.

12. The process of claim 11 wherein the silicone compound has the formula:



wherein:

5 M is $R^1_3SiO_{1/2}$;

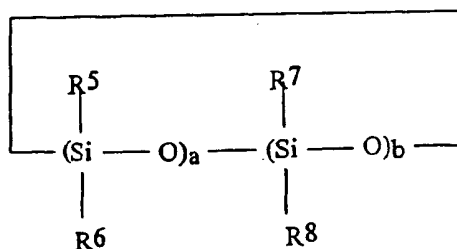
D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

10 R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical having from one to forty carbon atoms; and x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

13. The process of claim 11 wherein the silicone compound has the formula:



15 wherein:

R^5 , R^6 , R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

INTERNATIONAL SEARCH REPORT

onal Application No

PCT/US 02/04620

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06L1/02 D06L1/04 C11D11/00 D06F43/00 C11D7/50
//C11D3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06L C11D D06F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 197826 Derwent Publications Ltd., London, GB; Class A26, AN 1978-46701A XP002206086 & JP 53 056203 A (LION FAT & OIL CO LTD), 22 May 1978 (1978-05-22) abstract	1,2,4,6, 8,10-12, 14,16,18
X	US 5 834 416 A (MORGAN DAVID LEE ET AL) 10 November 1998 (1998-11-10) column 6, line 44 - line 53 claims 1,2	10-12, 14,16,18
X	WO 99 10587 A (LAUBACH BERNADETTE STOREY ;MICELL TECHNOLOGIES (US); DEYOUNG JAMES) 4 March 1999 (1999-03-04) page 8, line 1 - line 32	1,10,11

-/--



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

16 July 2002

Date of mailing of the international search report

29/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

US 02/04620

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5676705	A	14-10-1997	AU 4942996 A	23-09-1996
			CA 2211412 A1	12-09-1996
			WO 9627704 A1	12-09-1996
			EP 0813628 A1	29-12-1997
			FI 973603 A	05-09-1997
			TR 9700901 T1	21-02-1998
			US 5683473 A	04-11-1997
			ZA 9601786 A	05-09-1997
US 2002004953	A1	17-01-2002	WO 0250366 A1	27-06-2002
US 4685930	A	11-08-1987	AU 585906 B2	29-06-1989
			AU 4981785 A	22-05-1986
			CA 1239326 A1	19-07-1988
			DE 3583377 D1	08-08-1991
			EP 0182583 A2	28-05-1986
			JP 1502875 C	28-06-1989
			JP 61119765 A	06-06-1986
			JP 63050463 B	07-10-1988
US 5942007	A	24-08-1999	US 5865852 A	02-02-1999
			AT 215631 T	15-04-2002
			AU 4993599 A	07-02-2000
			AU 5101799 A	07-02-2000
			BR 9912088 A	10-04-2001
			BR 9912811 A	02-05-2001
			CN 1309733 T	22-08-2001
			CN 1309734 T	22-08-2001
			DE 69901179 D1	08-05-2002
			DK 1084289 T3	24-06-2002
			EP 1084289 A1	21-03-2001
			EP 1092056 A1	18-04-2001
			HU 0102648 A2	28-12-2001
			NO 20010231 A	14-03-2001
			NO 20010232 A	14-03-2001
			PL 345504 A1	17-12-2001
			PL 345509 A1	17-12-2001
			TR 200100312 T2	23-07-2001
			TR 200100318 T2	21-08-2001
			WO 0004221 A1	27-01-2000
			WO 0004222 A1	27-01-2000
			US 6063135 A	16-05-2000
			US 6042617 A	28-03-2000
			US 6056789 A	02-05-2000
			US 6042618 A	28-03-2000
			US 6086635 A	11-07-2000
			US 6059845 A	09-05-2000

INTERNATIONAL SEARCH REPORT

b .onal Application No

PCT/US 02/04620

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 685 930 A (KASPRZAK KENNETH A) 11 August 1987 (1987-08-11) cited in the application claims 1-9	1-19
A	US 5 942 007 A (BERNDT DIETER R ET AL) 24 August 1999 (1999-08-24) cited in the application claims 1-24	1-19

